



Sodium Titanates as Anodes for Sodium Ion Batteries

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To enable dual intercalation batteries based on sodium instead of lithium, anode materials other than graphite must be identified and developed. The most reliable materials will almost certainly be intercalation electrodes, because alloying processes with sodium involve very large volume changes not conducive to reversible cycling.¹ Very few materials insert alkali metal cations at sufficiently low potentials to be useful as negative electrodes; examples for Li ion battery applications include graphite, $\text{Li}_4\text{Ti}_5\text{O}_{12}$, and the recently discovered $\text{Li}_{1+x}\text{V}_{1-x}\text{O}_2$.² Sodium does not insert into graphite, but does undergo an unusual 3-phase reductive intercalation reaction with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ at about 1 V vs. Na^+/Na .³ Somewhat surprisingly, several sodium titanate compounds have recently been shown to undergo reversible sodium insertion reactions at potentials well below this value, making them of extreme interest for battery applications. These include $\text{Na}_2\text{Ti}_3\text{O}_7$,⁴ electrodes derived from $\text{NaTi}_3\text{O}_6(\text{OH}) \cdot 2\text{H}_2\text{O}$ (also known as sodium nonatitanate),⁵ and titanates with lepidocrocite structures.⁶ These materials all have stepped layered or corrugated structures, with sodium ions located between transition metal oxide layers, yet display distinctly different electrochemical behaviors in sodium cells. $\text{Na}_2\text{Ti}_3\text{O}_7$ exhibits a two-phase insertion reaction with a flat voltage profile at about 0.3V vs. Na^+/Na , whereas solid solution behavior is exhibited by sodium nonatitanate, as evidenced by the somewhat sloping voltage profile at an average cell potential of about 0.3V. The discharge profiles of the lepidocrocite-type titanates resemble that of the sodium nonatitanate electrode (although at slightly higher potentials) and XRD evidence suggests that solvent from the electrolytic solution is involved in the insertion mechanism. The widely varying electrochemical characteristics of these interesting titanate structures and what they imply for the future of sodium ion batteries will be discussed in detail during this presentation.

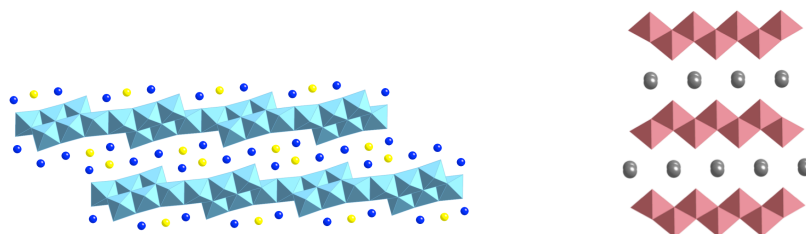
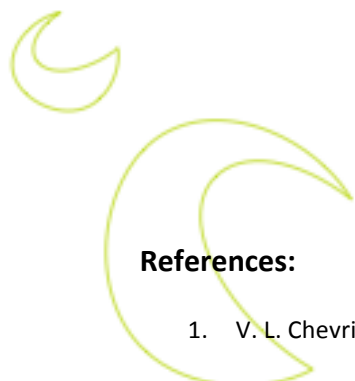


Figure 1. (left) structure of sodium nonatitanate, (right) corrugated structure of lepidocrocite titanate.

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